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THE CRYSTAL STRUCTURE OF β-ISOPRENE SULPHONE.

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A detailed X-ray analysis has shown that the molecule of β-isoprene sulphone has a heterocyclic structure in which resonance occurs between the three carbon-carbon bonds of the C_4S ring. The bond lengths are C—C (in the ring) 1·41 A., C (ring)—C (methyl) 1·54 A., C—S 1·75 A., and S—O 1·44 A., all ± 0·02 A.; the distribution of the four sulphur bonds is approximately tetrahedal.

It is not possible to determine the structure of crystalline rubber uniquely and exactly from the data of X-ray fibre diagrams alone. These data must therefore be very largely supplemented in other ways by accurate information from which the bond lengths and valency angles in the primary poly-isoprene chain and the probable relative disposition of atoms in neighbouring chains can be inferred.

To obtain this information it is proposed to make a systematic study of the crystal structures of relatively simple compounds containing isoprene units or atomic groupings related to isoprene, and the present paper contains the results of the first investigation of this series, on β-isoprene sulphone. This substance was chosen because the presence of the relatively heavy sulphur atom made it possible to carry out a detailed and accurate analysis without undue labour, and because, in view of the technical importance of vulcanisation, it was desirable to investigate a simple system containing sulphur attached to an isoprene unit. It was also hoped to establish the structure of this sulphone entirely independently of purely chemical evidence, on account of its importance as a representative of a large class of compounds of sulphur dioxide with conjugated dienes.

By crystallographic examination of β-isoprene sulphone Sauter[1] gave for the cell dimensions $a = 6{\cdot}60$, $b = 7{\cdot}62$ and $c = 6{\cdot}67$ A.; $\beta = 110° 34'$, and reported the space-group as $P2_1$. Our independent measurements of the unit cell are $a = 6{\cdot}77$, $b = 7{\cdot}72$, $c = 6{\cdot}70$ A., $\beta = 110° 42'$.

There are two molecules of $C_5H_8O_2S$ in the unit cell. The only systematic extinctions are (*oko*) absent for k odd, so that the space-group may be either $P2_1$ or $P2_1/m$. The results of the F^2 syntheses (see below) strongly suggested the latter, and this was assumed for the subsequent F syntheses. The final result fully substantiated this assumption.

The structure amplitudes of 454 planes were obtained experimentally from relative intensity measurements on oscillation photographs taken about the principle axes, coupled with absolute intensity measurements on selected planes. These amplitudes were used to carry out three

[1] *Z. Krist.*, 1932, 83, 340.

dimensional F^2 (Patterson) Fourier syntheses for $y = 0$ and $y = 1/2$, the appropriate formulæ being:

$$P_{xoz} = 4 \sum_{-H}^{H} \sum_{0}^{L} \left[\sum_{0}^{K} F^2_{hkl} \right] \cos 2\pi(hx + lz).$$

and

$$P_{x\frac{1}{2}z} = 4 \sum_{-H}^{H} \sum_{0}^{L} \left[\sum_{0}^{K} F^2_{hkl}(-1)^k \right] \cos 2\pi(hx + lz).$$

These summations and the subsequent F-syntheses were effected by the method of Beevers and Lipson;[2] the results are shown in Figs. 1 and 2 with skeleton molecular formulæ superimposed.

The height of a peak in an F^2 synthesis is determined approximately by the product of the atomic numbers of the two atoms which give rise to the peak: in the present case, therefore, it is to be expected that

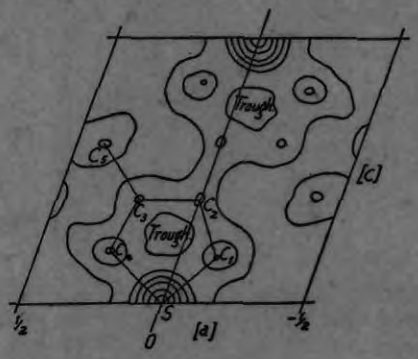


FIG. 1.

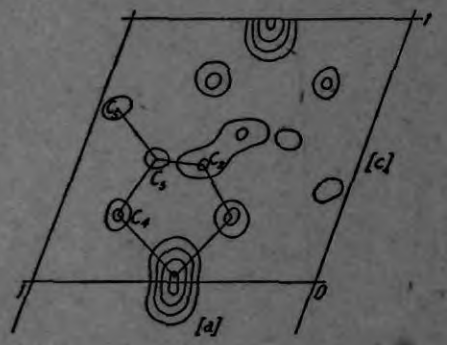


FIG. 2.

the S—S peaks will be outstanding and that the C—C peaks will probably be negligible by comparison with S—C and S—O peaks.

Owing to the presence of a two-fold screw axis of symmetry, the S—S peaks must occur in the F^2 synthesis at $y = 1/2$, and they can be identified without difficulty in Fig. 2. Apart from the large peak at the origin in Fig. 1 (which is merely an expression of the fact that every atom is at zero distance from itself) all the remaining peaks of any magnitude in both sections are of about the same height, and as the superimposed skeleton formulæ show, they can be identified as C—S peaks. If these identifications are correct the structure is thus built up of molecules in which the terminal atoms of the isoprene chain have been linked to sulphur to form a heterocyclic ring, as previously assumed by organic chemists. The fact that all the peaks expected from C—S distances appear in the two sections, and are all of about the same height, shows that the C_4S ring is approximately planar, and parallel to the crystallographic (010) plane. No peaks appear in Figs. 1 and 2 which might be associated with S—O distances and indeed if, as would seem probable, the oxygen atoms are attached to the sulphur atom in such a way as to give a tetrahedal distribution of the four sulphur valencies; then a S—O peak should appear at about $y = 1/12$. A section of the F^2-synthesis was made at $y = 1/12$ and a peak of appropriate height was

[2] *Phil. Mag.*, 1934, **17**, 855.

found; its y co-ordinate was determined more exactly by a line synthesis parallel to the b-axis.

The approximate co-ordinates deduced from these F^2-syntheses (taking into account the best available data on bond lengths) were used to calculate the structure factors of all planes with a spacing greater than 1·5 A. As the agreement with the experimental values was satisfactory, the latter were given the phase angles (integral multiples of $\pi/2$) obtained in the calculations, and electron densities were evaluated by means of three-dimensional syntheses over appropriate regions in the unit cell. Successive structure factor calculations and syntheses, introducing all the available terms, were made; the result of the sixth and final synthesis is given in Fig. 3, which shows the section at $y = \frac{1}{4}$, with the section at $y = 0{\cdot}095$ inset. The contours are drawn at intervals of one electron/A^3 (the zero contour being omitted), except in the case of the sulphur atom, where the interval between the contours is two electrons/A^3.

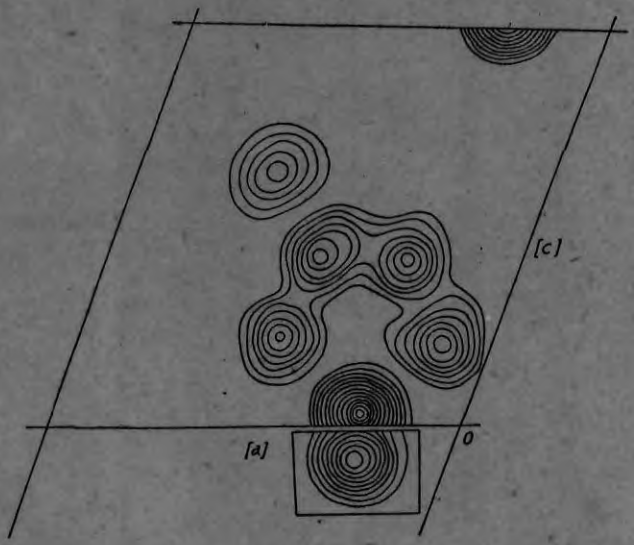


FIG. 3.

The final co-ordinates are given in Table I.

TABLE I

	x.	y.	z.
S	0·262	0·250	0·031
C_1	0·120	0·250	0·203
C_2	0·276	0·250	0·408
C_3	0·490	0·250	0·424
C_4	0·520	0·250	0·226
C_5	0·678	0·250	0·639
O	0·226	0·095	−0·095

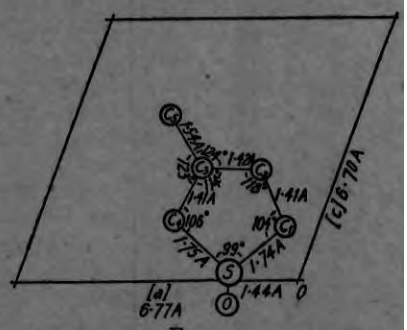


FIG. 4.

The mean difference between these co-ordinates and those deduced from the penultimate synthesis is 0·0018, corresponding to about 0·013 A. The experimental structure factors are compared diagrammatically in Fig. 5 with the values calculated from the above final co-ordinates.

The general agreement shown in this diagram is satisfactory, indicating the correctness of the interpretation of the syntheses, and confirming

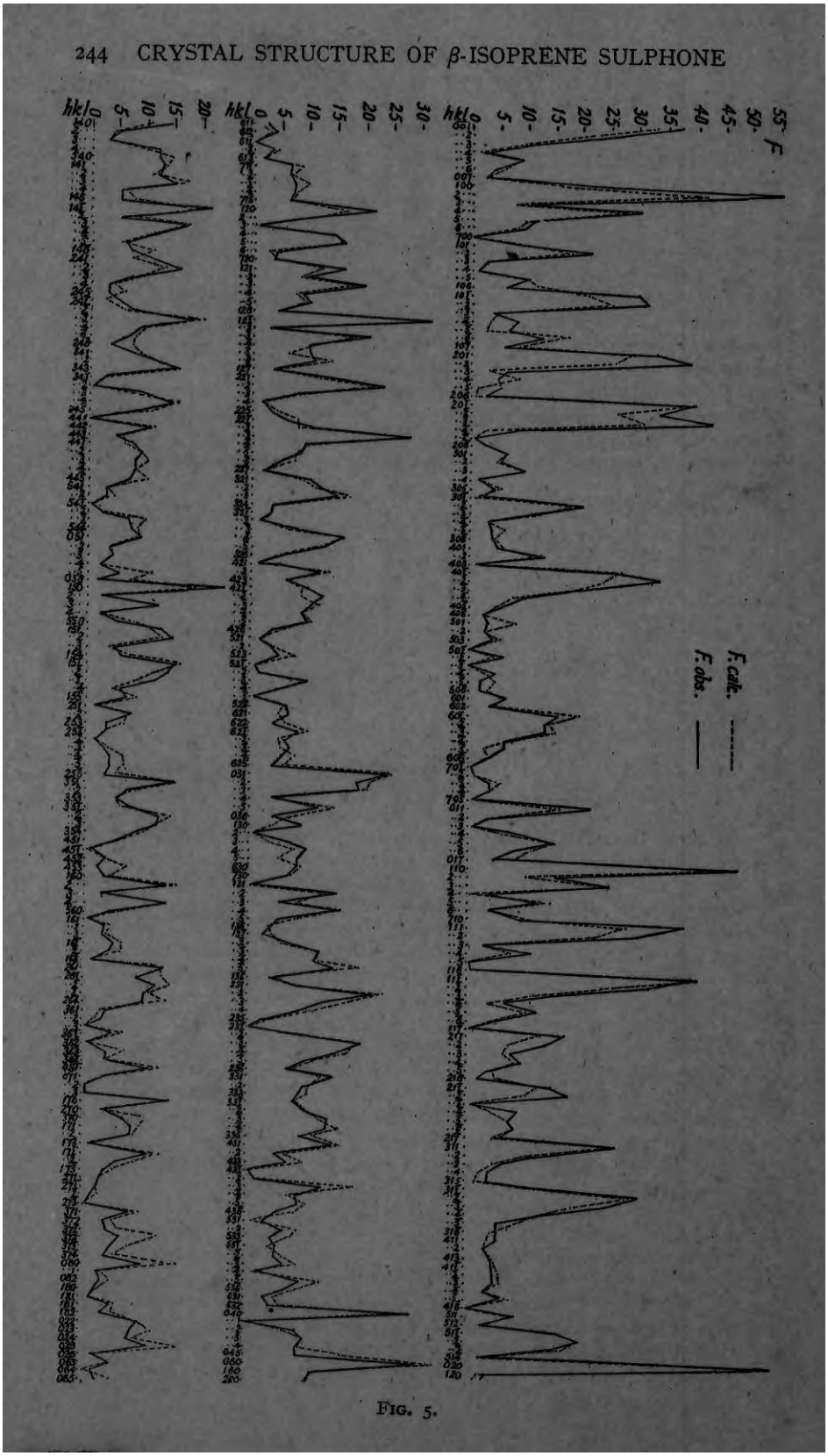


FIG. 5.

the validity of the assumption that the molecules lie in the planes of symmetry of the space-group $P2_1/m$. A more searching test of this assumption was made as follows: any small displacement of atoms out of the symmetry planes will have the smallest effect on (*hol*) structure factors, and the largest effect on structure factors of planes with high values of k; accordingly, the differences between $F_{calc.}$ and $F_{obs.}$ were averaged first for thirty (*hol*) planes, and secondly, for an equal number of planes with k greater than 5. In the first case the mean difference was found to be 2·10, and in the second case only 2·00; it is therefore inferred that within the limits of accuracy of the analysis the molecules possess planes of symmetry and the space-group is $P2_1/m$.

The interatomic distances and valency angles derived from the final co-ordinates are given below, and a diagram of the molecule is shown in Fig. 4. As a result of the symmetry the two S—O distances are equal and the angle O—S—O is bisected by the plane of the carbon atoms.

TABLE II

S—C_1	1·74 A.	C_1—S—C_4	99°
S—C_2	1·75	O—S—O	112 1/2
S—O	1·44	S—C_1—C_2	104 1/2
C_1—C_2	1·41	S—C_4—C_3	105 1/2
C_2—C_3	1·42	C_1—C_2—C_3	117 1/2
C_3—C_4	1·41	C_2—C_3—C_4	113 1/2
C_3—C_5 (methyl)	1·54	C_2—C_3—C_5	123 1/2
		C_4—C_3—C_5	123

The shorter intermolecular distances are:

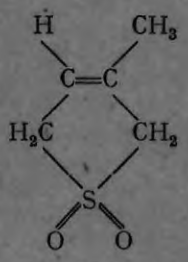
C_3——O 3·71 A., O——O 3·93 A., O——C_1 3·45 A.
C_5——C_2 3·89 A., C_5——C_3 4·00 A., and C_3——C_3 4·00 A.

Of these, the first is between molecules in the same plane and the others are between molecules in planes $1/2b$ apart.

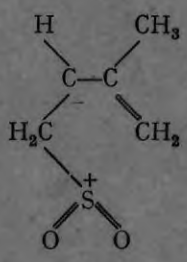
The interatomic distances given above are considered to be accurate to about 0·02 A., and the angles to 2°. The sulphur-oxygen distance is in good agreement with other recent X-ray and electron diffraction values, *e.g.* 1·44 ± 0·03 A. in potassium sulphamate,[3] 1·45 ± 0·02 A. in thionyl chloride, and 1·43 ± 0·02 A. in sulphuryl chloride,[4] and the sulphur valency angles are roughly tetrahedal as would be expected. The S—C bonds are rather shorter than the sum of the usually accepted single bond radii (1·81 A.) and although the C_3—C_5 (methyl) bond is exactly that to be expected for a single bond, the other carbon-carbon distances are considerably shorter; thus while the bonds external to the heterocyclic ring are normal, all those in the ring are intermediate in length between single and double bonds.

Although the evidence could not be regarded as entirely satisfactory, β-isoprene sulphone has been ascribed the structure I on chemical grounds.[5]

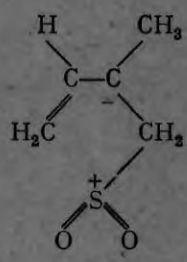
[3] Cox and Brown, *J.C.S.*, 1940, 1.
[4] Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.
[5] See *e.g.*, Boeseken and van Zuydewijn, *Proc. K. Akad, Wetensch, Amsterdam*, 1934, **37**, 760; 1937, **40**, 23; *Rec. Trav. Chim.*, 1937, **56**, 1047; 1938, **57**, 445; and Backer, Strating and Zuithoff, *ibid.*, 1936, **55**, 761.



I.



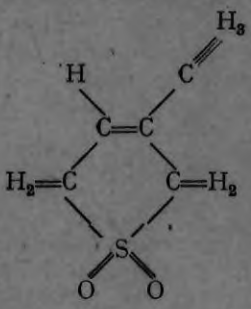
II.



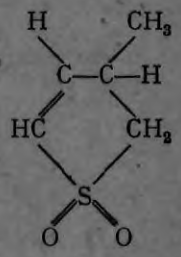
III.

If the bond lengths reported above are accepted, it is clear that I does not adequately represent the structure since it would require two single carbon-carbon bonds of length about 1·54 A., and one double bond of about 1·34 A. in the ring; the notable feature of the experimental results is that these three bonds are equal within the errors of measurement, and of length intermediate between single and double bonds. We therefore suggest that β-isoprene sulphone has a structure involving resonance between I and the ionised forms II and III in approximately equal measure; equal contributions from these three forms would be expected to give three equal C—C bonds of about 1·43 A. in length, each possessing about 33 % double bond character. The formulation of the sulphone as a resonance structure involves a type of valency binding which is rather uncommon among organic compounds, but which is similar to that supposed to exist in other sulphur compounds.[6]

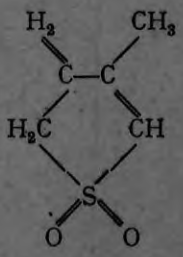
The structure now suggested implies that the C—S bonds will be approximately two-thirds single bond and one-third semi-ionic in character, and it is difficult to predict what effect this will have on the interatomic distance; the observed value is about 0·06 A. less than the predicted single-bond distance.



IV.



V.



VI.

If I is written in the form IV it will be observed that there is the possibility of "hyperconjugation,"[7] and it is conceivable that this may account in some measure for the observed results, although the normal value of 1·54 A. obtained for the C—C (methyl) bond length is against this.

It was shown by Eigenberger[8] that when the normal or β-form of isoprene sulphone is treated with aqueous or alcoholic potassium

[6] See, *e.g.*, Pauling, *The Nature of the Chemical Bond*, pp. 221 *et seq.*
[7] Mulliken, Rieke and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41.
[8] J. *pr. Chem.*, (ii), 1931, **129**, 312, 326.

hydroxide in ultra-violet light it is converted into an equilibrium mixture containing about 8 % of the original substance and 92 % of a new compound of identical analysis and molecular weight, but different chemical and physical properties.

Boeseken and van Zuydewijn [5] and Backer *et al.* [5] have suggested that this new substance, which is called α-isoprene sulphone, is an isomer with the structure V or VI.

A preliminary X-ray examination of this substance was made, and its monomeric character was confirmed, but a detailed analysis was not considered to be justified at the present time. It is of interest to note that if the hydrogen atoms in α-isoprene sulphone are attached to the carbon atoms, as indicated in V or VI, it is impossible to formulate ionised structures similar to II and III without transgressing the octet rule for at least one carbon atom, and a resonance structure is not to be expected. Hyperconjugation effects, on the other hand, would be expected to be quite as marked in VI as in IV. It is hoped to investigate the α-form in more detail later.

In view of the somewhat unexpected nature of the structure of β-isoprene sulphone, it is uncertain how far the results are directly applicable to isoprene units in "crystalline" rubber. Its structure, however, may well have some bearing on certain rubber problems, and it is interesting to note that structures involving comparable C_4S rings have been proposed for ebonite.[9]

The above work has been carried out as part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

In order to meet the need for economy in the use of paper, full numerical tables of observed and calculated values have been omitted. The experimental portion of the paper has also been omitted, but the original draft may be inspected by any member of the Society who is interested, on application to the Secretary.

Summary.

A detailed X-ray analysis has shown that the molecule of β-isoprene sulphone has a heterocyclic structure in which resonance occurs between the three carbon-carbon bonds of the C_4S ring. The bond lengths are C—C (in the ring) 1·41 A., C (ring)—C (methyl) 1·54 A., C—S 1·75 A., and S—O 1·44 A., all ± 0·02 A.; the distribution of the four sulphur bonds is approximately tetrahedal.

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[9] See, *e.g.*, Medgeley, Henne and Sheppard, *Rubber Chem. and Tech.*, 1934, 1, 520.

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